REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
21-03-2012

2. REPORT TYPE
Briefing Charts

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE

Influence of Peripheral Architecture on the Properties of Aryl Polyhedral Oligomeric Silsesquioxanes

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
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5d. PROJECT NUMBER

5f. WORK UNIT NUMBER
23030521

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

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10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)
AFRL-RZ-ED-VG-2012-086

12. DISTRIBUTION / AVAILABILITY STATEMENT

Distribution A: Approved for public release; distribution unlimited. PA# 12211.

13. SUPPLEMENTARY NOTES
For presentation at the 243rd ACS National Meeting, San Diego, CA, 25-29 March 2012 and publication in Polymer Preprints, March 25, 2012.

14. ABSTRACT

POSS compounds with non-reactive, aryl functionality are difficult to disperse in host materials. Recently, several new POSS compounds featuring this type of periphery demonstrated enhanced solubility in solvents and polymers. The effect of peripheral architecture on macroscale properties of aryl POSS compounds is not well understood. POSS properties should be dependent on peripheral architecture, symmetry, and packing efficiency. The aim of this work is to correlate peripheral architecture to POSS assembly and measurable thermal properties.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Dr. Joseph M. Mabry
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER *(include area code)*
Unclassified	Unclassified	Unclassified	SAR	19	N/A

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Influence of Peripheral Architecture on the Properties of Aryl Polyhedral Oligomeric Silsesquioxanes

28 Mar 2012

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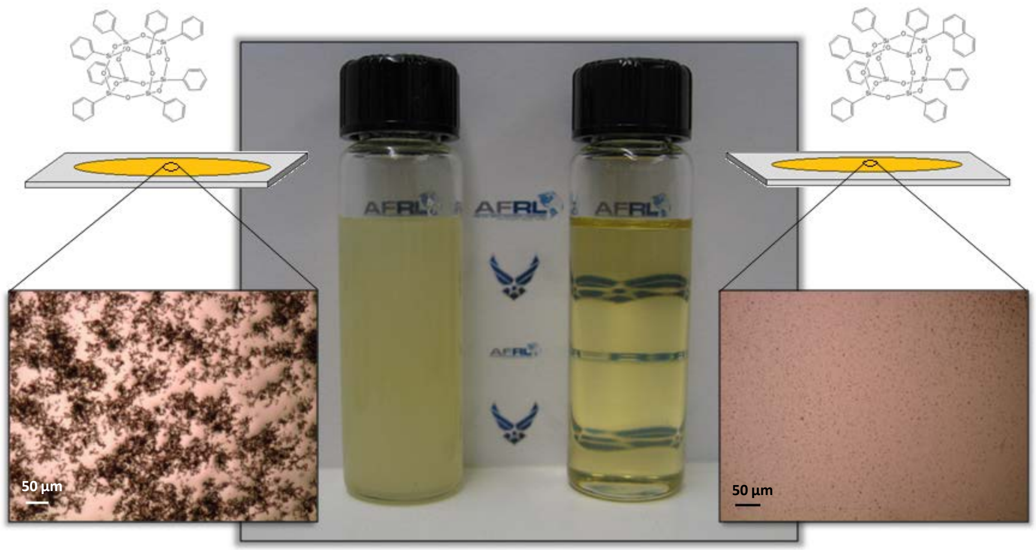
Background

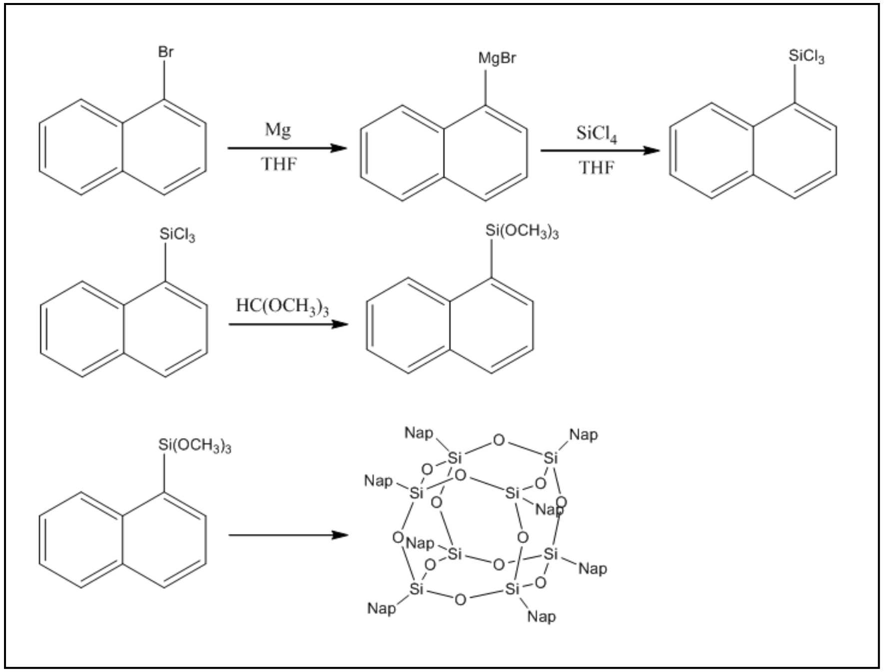


- Phenyl$_8$T$_8$ POSS and 1-Naphthyl-Phenyl$_7$ POSS were solubilized with Ultem 1000 in chloroform at 5 weight % POSS and 5 weight % solute
- Films subsequently cast and annealed
- The solution containing 1-Naphthyl-Phenyl$_7$ POSS is clear and the film exhibits reduced phase separation

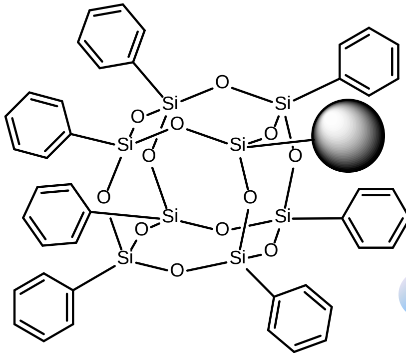
Journal of Organometallic Chemistry 696 (2011), pp. 2676-2680
DOI information: 10.1016/j.jorganchem.2011.03.035

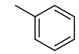
- POSS compounds with non-reactive, aryl functionality are difficult to disperse in host materials
- Recently, several new POSS compounds featuring this type of periphery demonstrated enhanced solubility in solvents and polymers
- The effects of peripheral architecture on macroscale properties of aryl POSS compounds are not well understood
- POSS properties should be dependent on peripheral architecture, symmetry, and packing efficiency
- The aim of this work is to correlate peripheral architecture to POSS assembly and measurable thermal properties

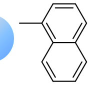
Synthesis of Ar-Functionalized POSS Compounds

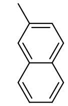


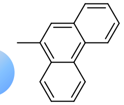
- Four symmetric T_8 compounds synthesized
- Four corner-capped T_8 compounds synthesized

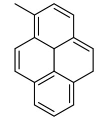


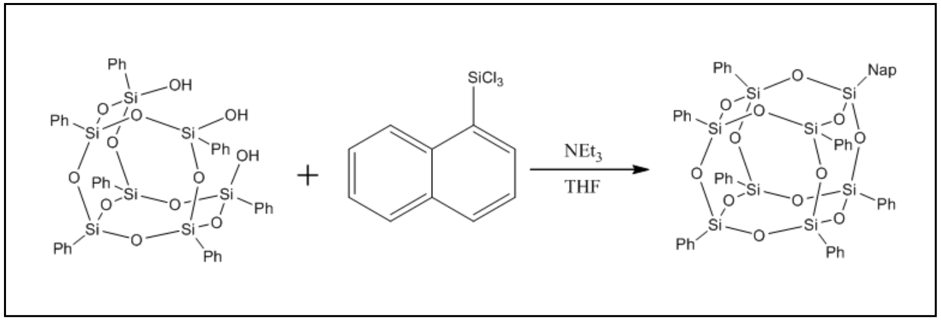
1  **Phenyl$_8$T$_8$**

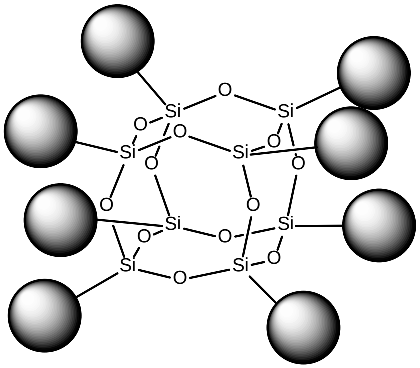
2  **1-Naphthyl-Phenyl$_7$T8**

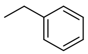
3  **2-Naphthyl-Phenyl$_7$T8**

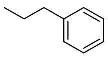
4  **9-Phenanthrenyl-Phenyl$_7$T8**

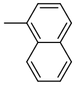
5  **1-Pyrenyl-Phenyl$_7$T8**



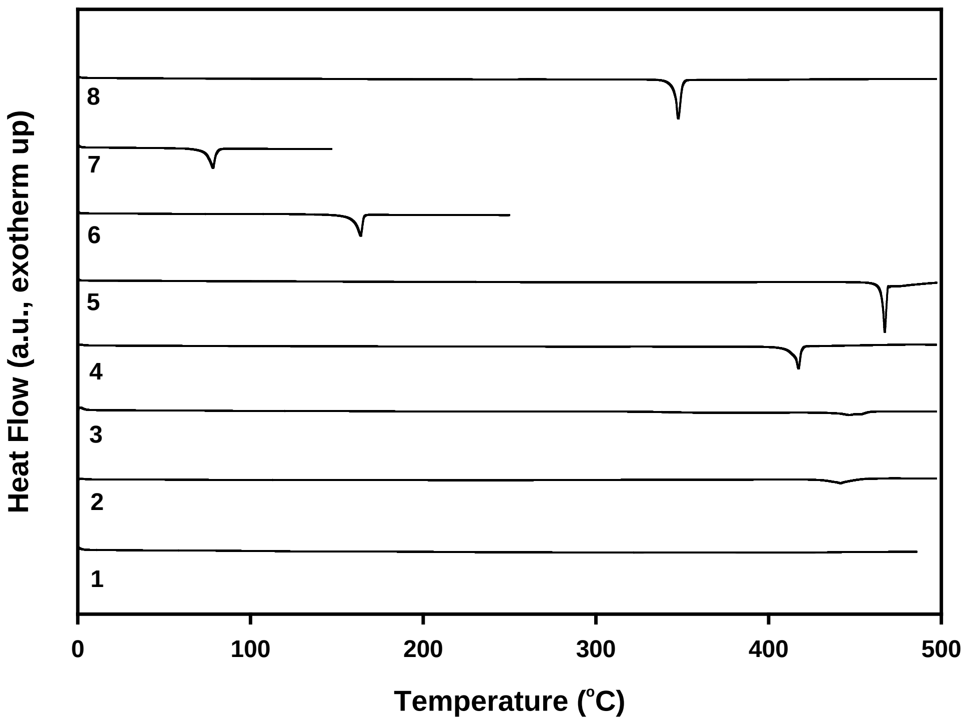


6  **Phenethyl$_8$T$_8$**

7  **Benzyl$_8$T$_8$**

8  **1-Naphthyl$_8$T$_8$**

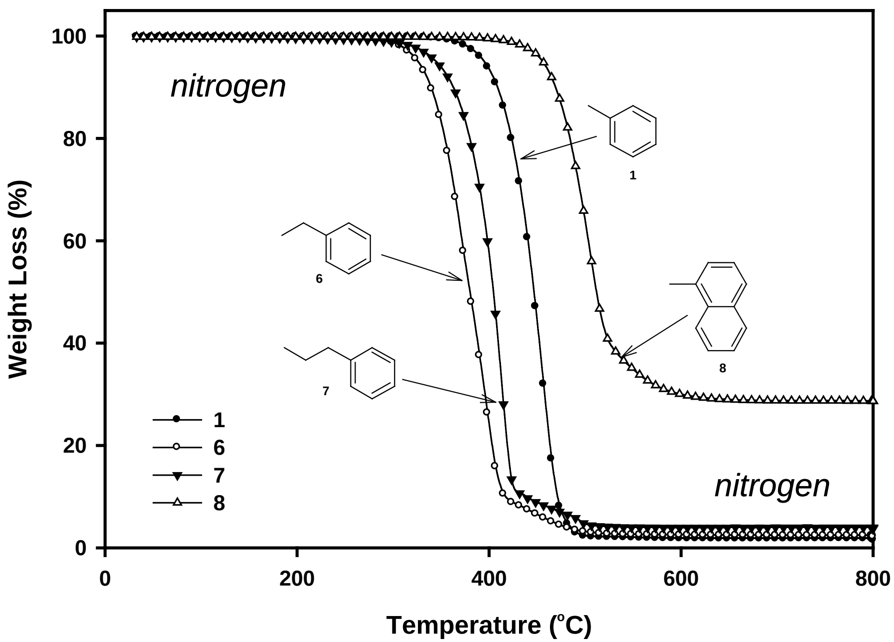
Standard DSC

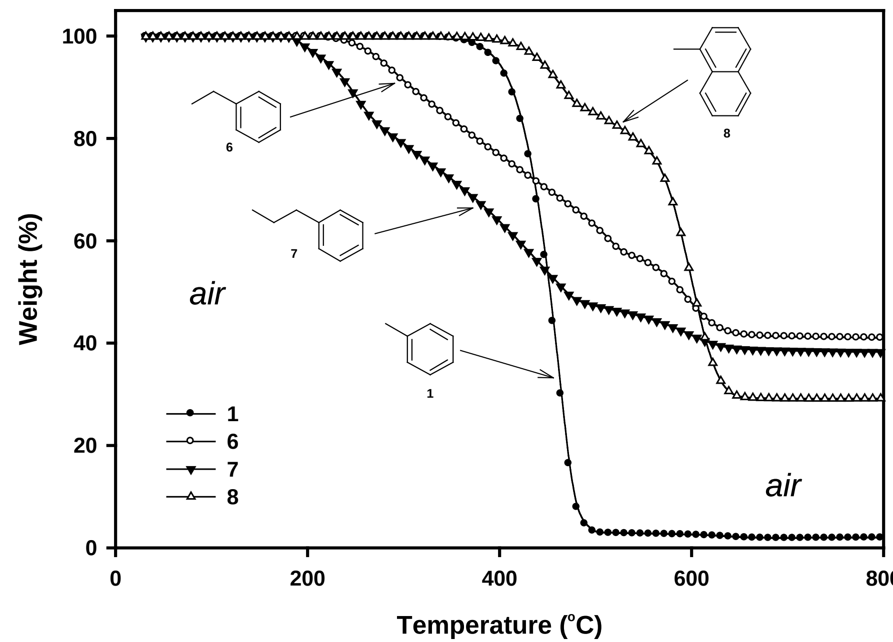


POSS	mp (°C)	ΔH (J/g)
1	n/a	n/a
2	442	26
3	447	20
4	416	47
5	467	59
6	164	52
7	78	44
8	348	69

- All compounds with the exception of 1 exhibit an endothermic peak
- 6 and 7 demonstrate relatively low melting points due to alkyl spacers in their organic peripheries

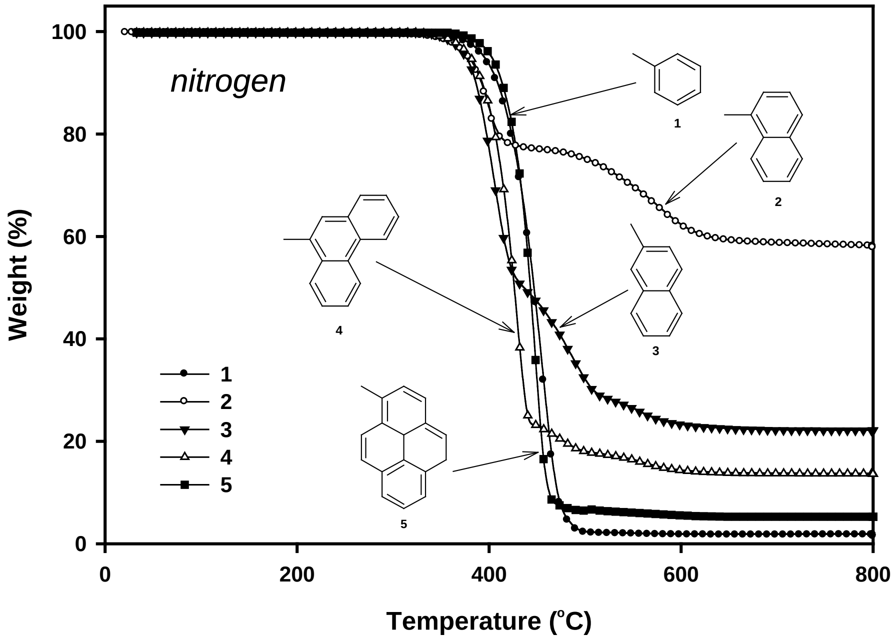
TGA of Symmetric Aryl POSS

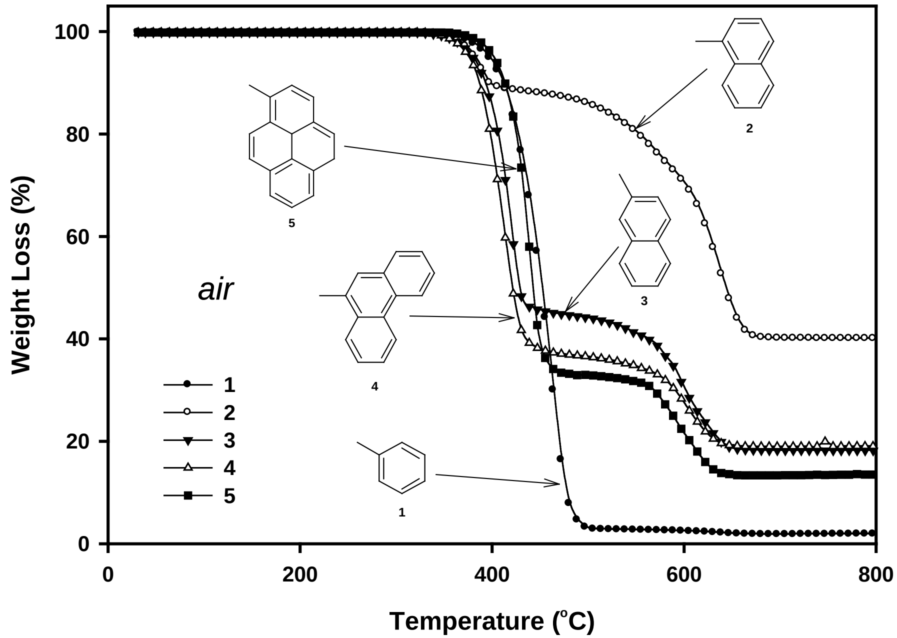




- Anaerobically, 1 & 6-8 demonstrate single-step weight loss in most cases leaving virtually no residue
- In an oxidizing atmosphere, 6-7 begin to lose mass at ~200°C due to peroxidation of alkyl spacers and a significant residual white residue remains for all of the compounds with the exception of 1
- Mass loss of 1 during TGA is insensitive to purge atmosphere

TGA of Asymmetric POSS

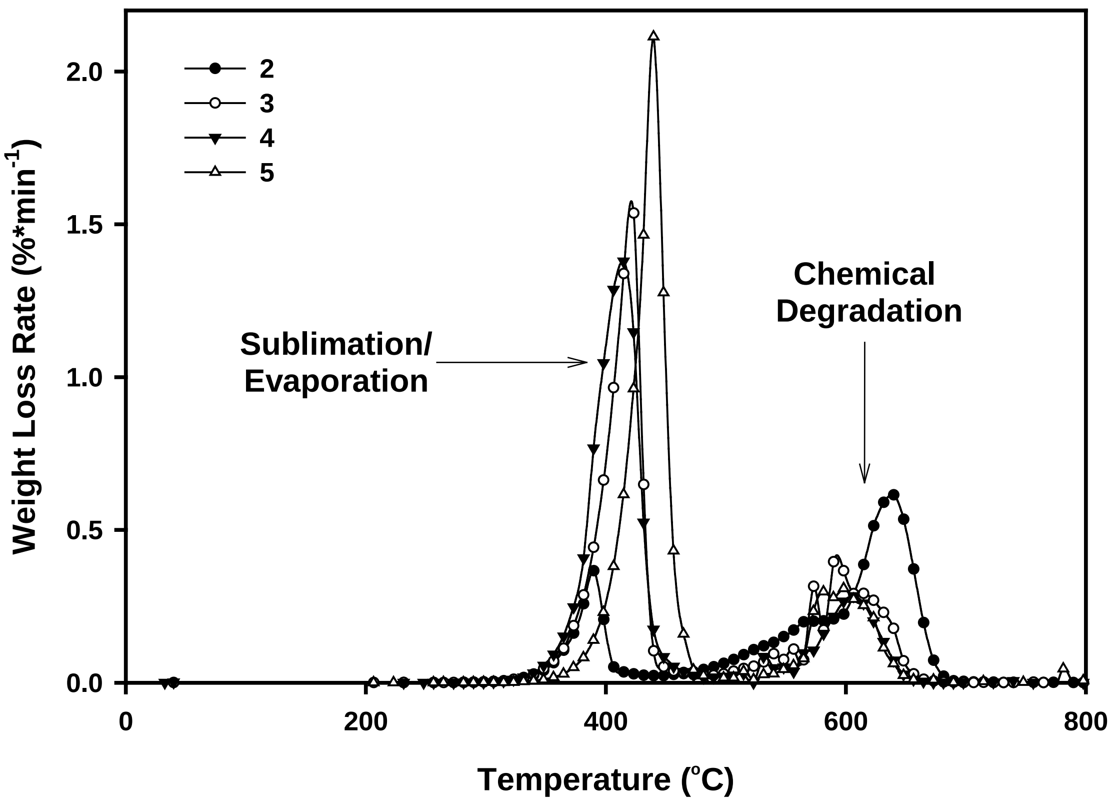




- Compounds 2-5 lose mass during two distinct events
- The magnitude of the first event appears to correlate with the geometric size of the corner cap species
- The first mass loss event for 4 and 5 is suppressed during decomposition in air likely due to activity of hydrogens on phenanthrene and pyrene groups

TGA of Asymmetric Aryl POSS

- **Plot of mass loss rate vs. T for 2-5 during aerobic decomposition highlights distinction between two events**
- **First event is postulated to be due to sublimation / evaporation, while the second may be attributed to physical degradation at high temperature**



TGA Mass Loss Statistics

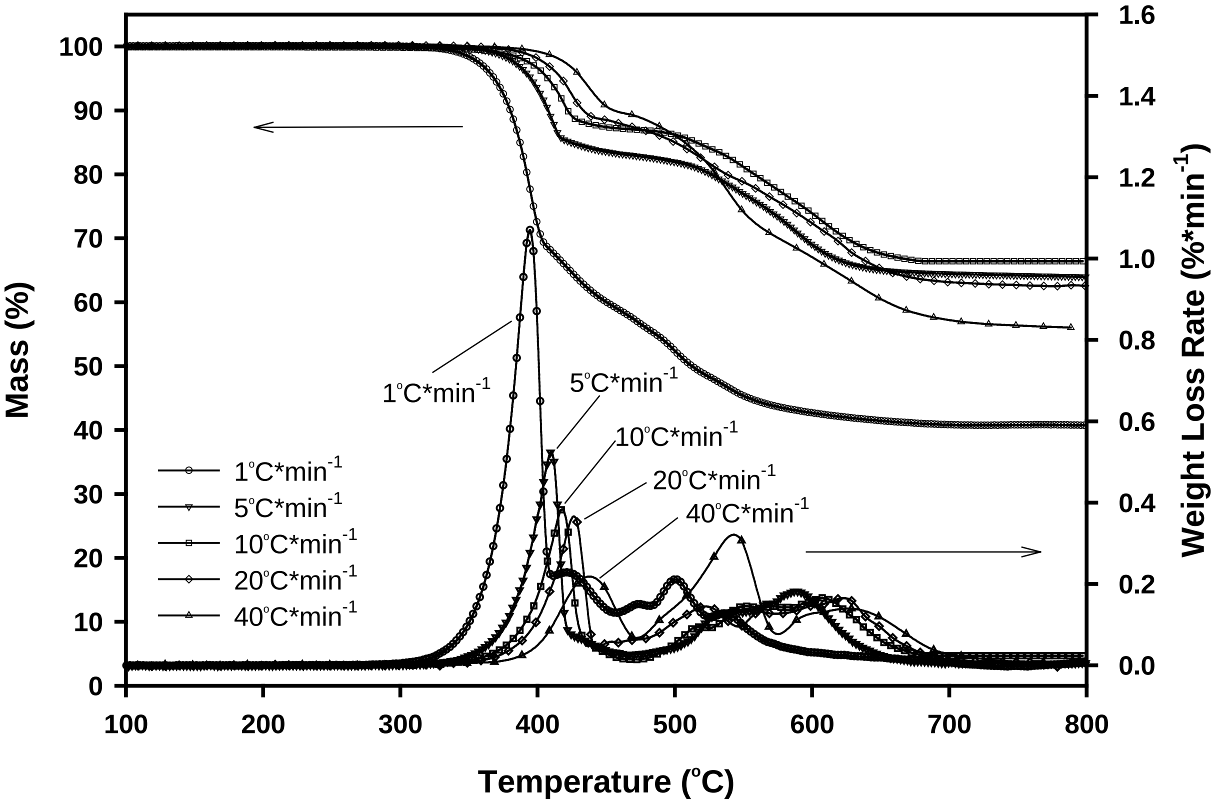
	ANAEROBIC DECOMPOSITION				AEROBIC DECOMPOSITION		
POSS	Residue (%)	Approx. Sub/Evap Loss (%)	SiO_2 Yield Theoretical† (%)	SiO_2 Yield Experimental (%)	Approx. Sub/Evap Loss (%)	SiO_2 Yield Theoretical (%)	SiO_2 Yield Experimental (%)
1	1.2	98.8	0.6	0.6	95.2	2.2	1.8
2	58.7	21.7	34.8	34.8	9.8	40.1	40.2
3	14.0	82.0	8.0	7.5	58.5	18.4	18.4
4	21.7	69.0	13.2	14.0	58.0	17.8	19.2
5	8.7	91.1	3.7	6.3	67.0	13.7	13.7
6	2.4	89.9	4.2	2.1	0.0	42.0	41.1
7	4.5	88.7	4.3	4.1	0.0	38.3	38.7
8	28.6	58.9	13.8	16.8	11.6	29.7	29.2

† Theoretical yield based on oxidation of residual POSS cage content after sublimation/evaporation

$$SiO_{2,theor.} = (M_i - M_s) \cdot \frac{416.8\ g/mol}{MW} \cdot 1.15355$$

- Assumption: cage loss occurs only during sublimation/evaporation events
- Statistics pertaining to SiO_2 formation support hypothesis that initial rapid mass loss events are largely attributed to sublimation/evaporation losses

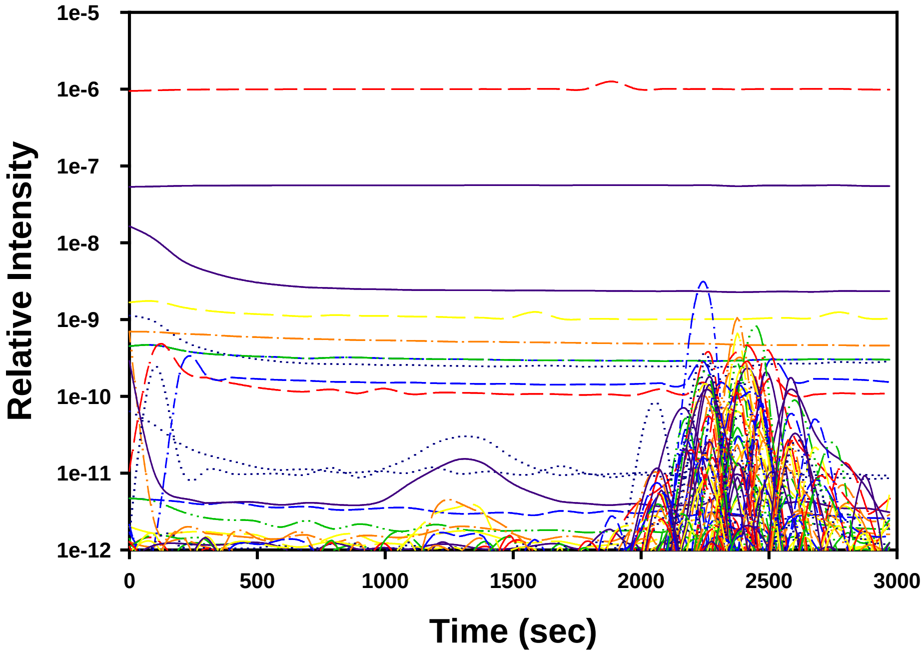
Effect of Heating Rate on Mass Loss

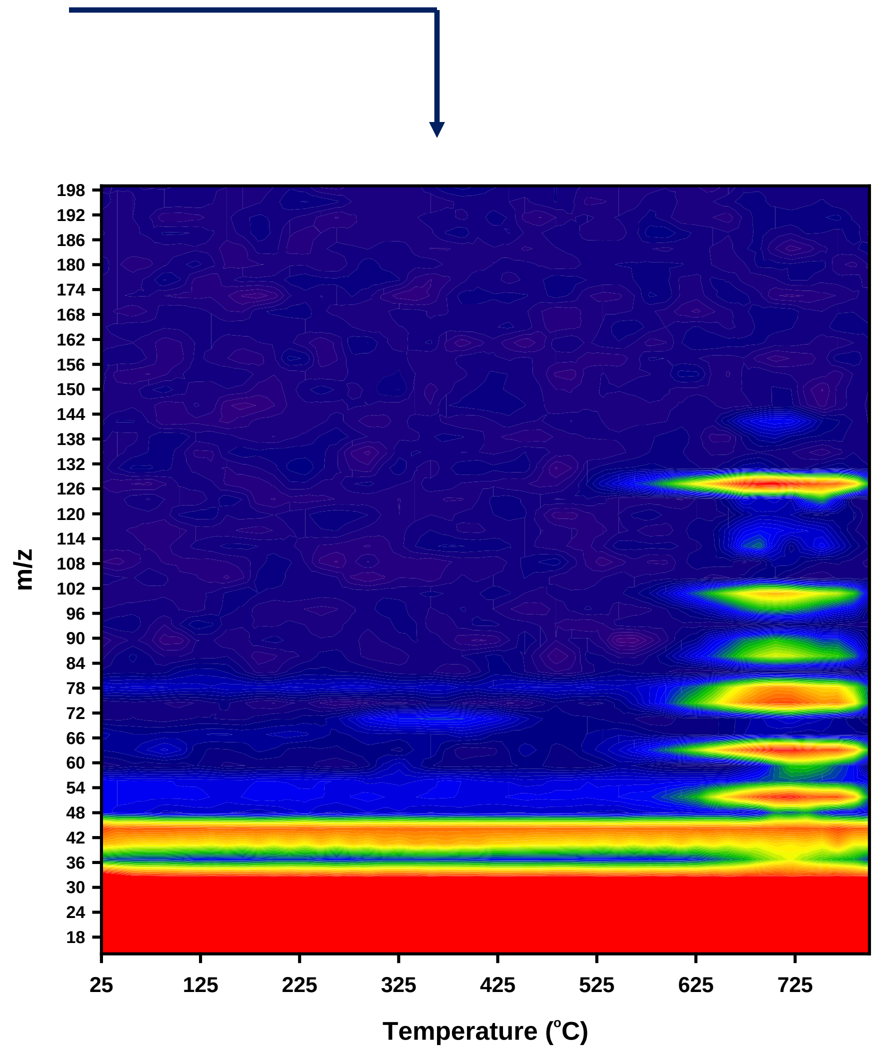


TGA analysis of 2 in nitrogen at different heating rates

- **TGA heating rate affects kinetics of mass loss**
- **Increasing the heating rate diminishes the intensity of the first mass loss event**
- **10°C·min^{-1} leaves highest residue**
- **Mass loss due to second event increases with heating rate above 10°C·min^{-1}**

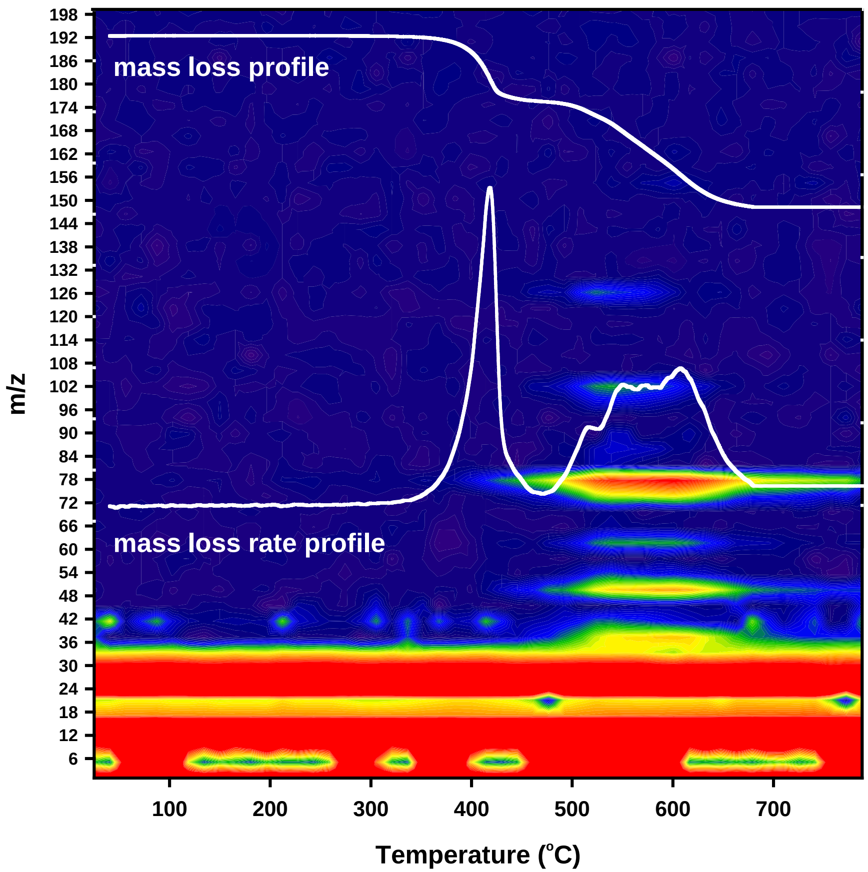
TGA-Mass Spectrometry

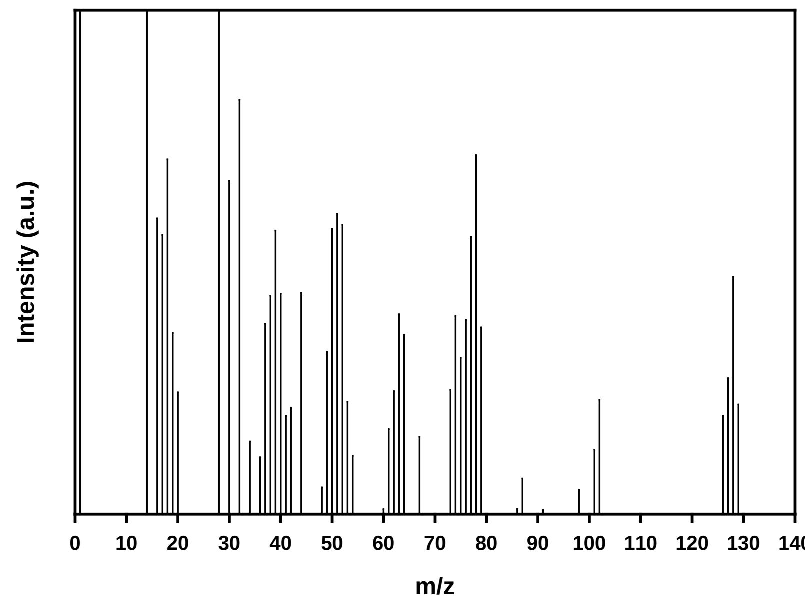




- Code developed to manipulate mass spectrometry data output into a 2D form of m/z vs. temperature during the TGA scan
- Use of helium or argon as the purge gas is preferable

TGA-Mass Spectrometry

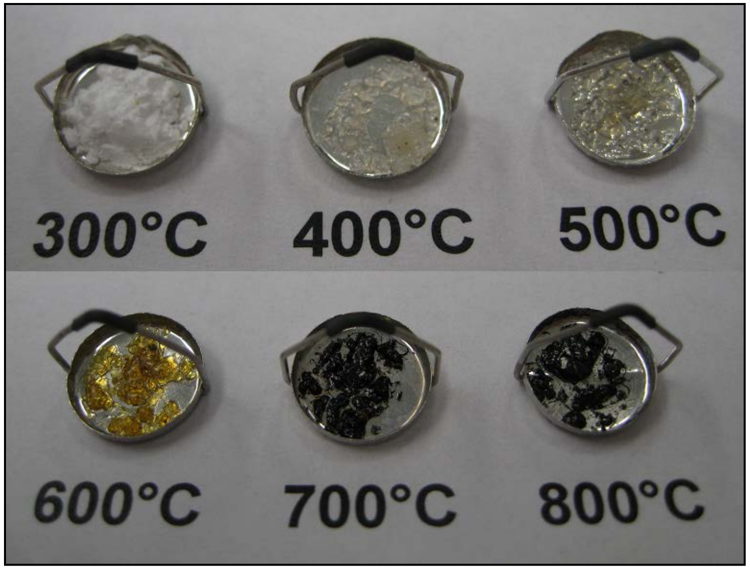




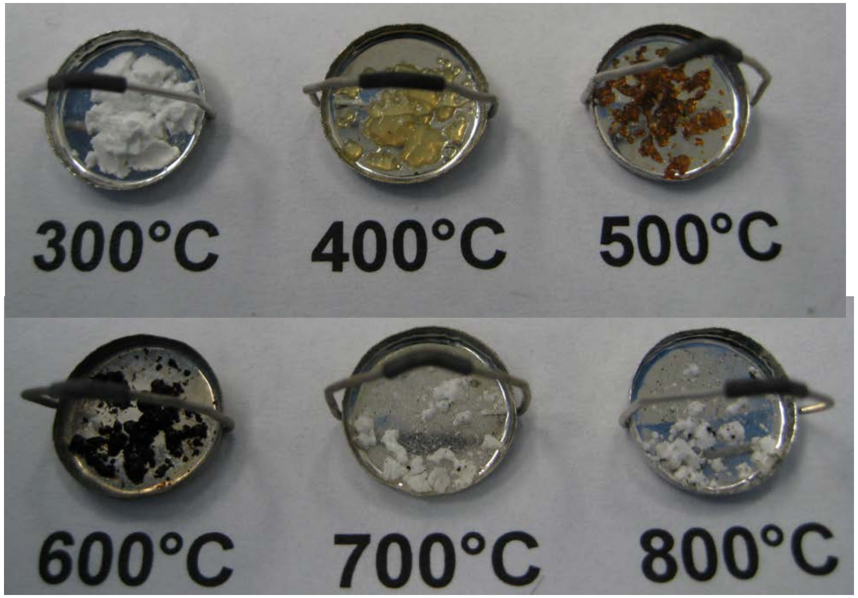
Snapshot of mass spectrum of **2** at 528°C

- **Data suggests chemical degradation occurs primarily through peripheral scission**
- **First mass loss event not detected, likely due to condensation of evaporated/sublimated POSS in capillary**

Residue Analysis



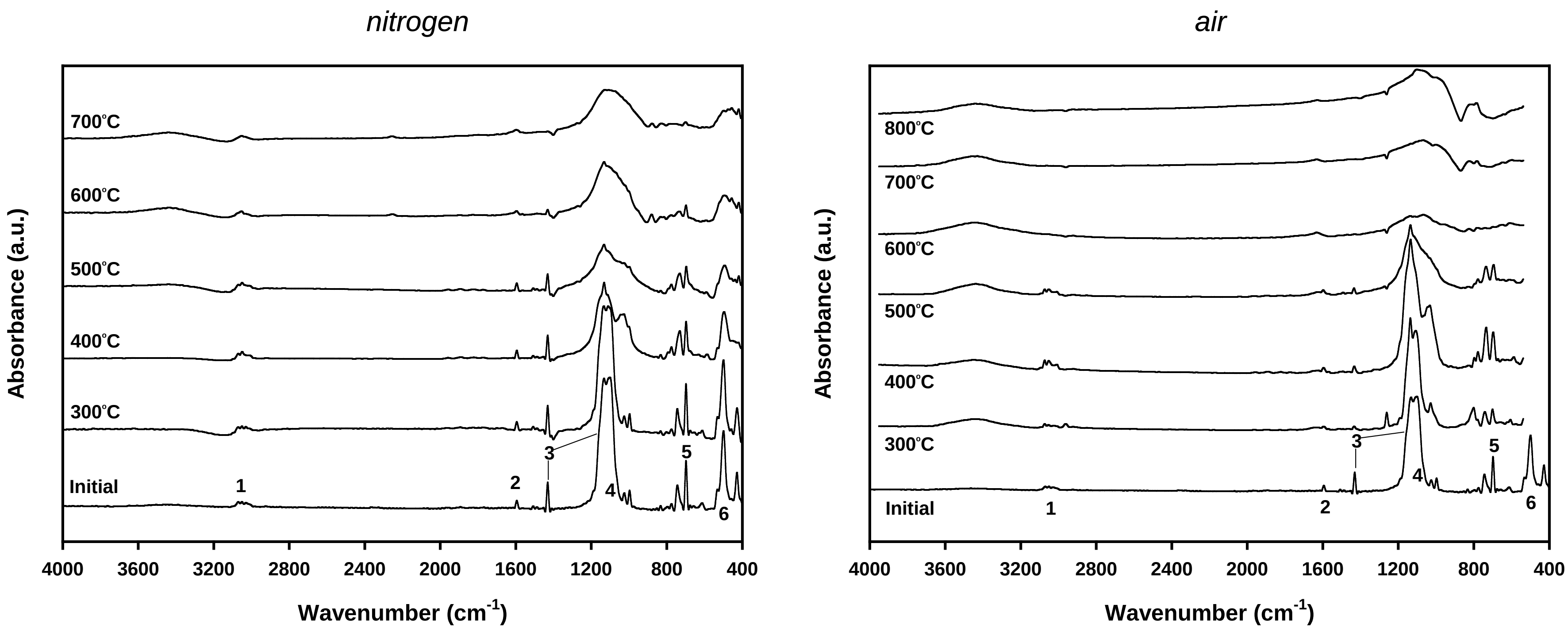
Inert Atmosphere



Oxidizing Atmosphere

- **10 mg samples of 2 heat treated at prescribed temperatures until equilibrium achieved**
- **Residues ground with KBr and analyzed in transmission by FTIR**

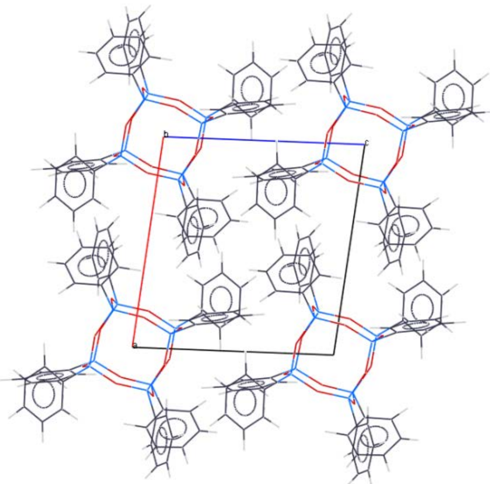
FTIR of 2 after Heat Treatment in Nitrogen and Air

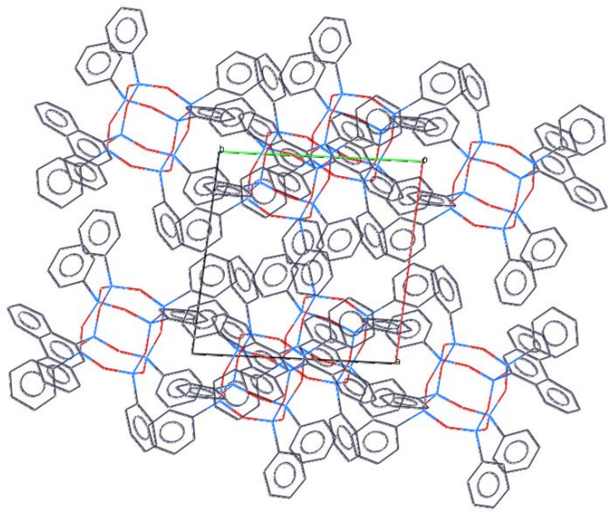


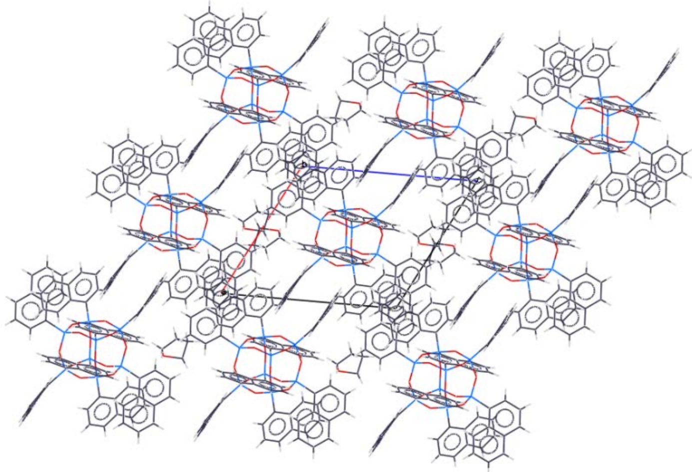
- **Spectra reveal that residue is partially organic after treatment at 700°C in nitrogen**
- **Residue appears to be completely SiO and SiO_2 after treatment at 600°C in air**

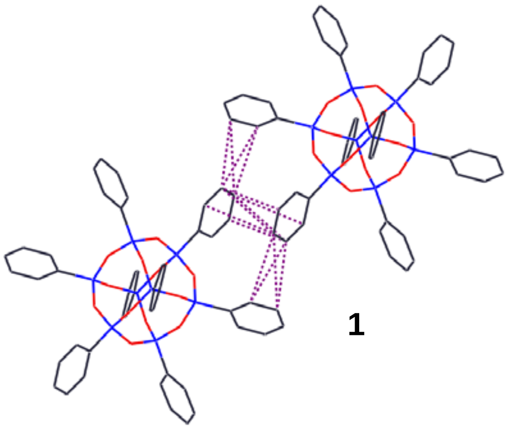
1 C-H Phenyl Asymmetric Stretching (3050 cm^{-1})
2 Aromatic C=C Asymmetric Stretching (1600 cm^{-1})
3 Si-Phenyl Deformation (1137 cm^{-1}, 1432 cm^{-1})
4 Si-O deformation (1100 cm^{-1})
5 Aromatic C-H Bending (700 cm^{-1})
6 Si-O-Si Out-of-Plane Bending (505 cm^{-1})

Single Crystal XRD

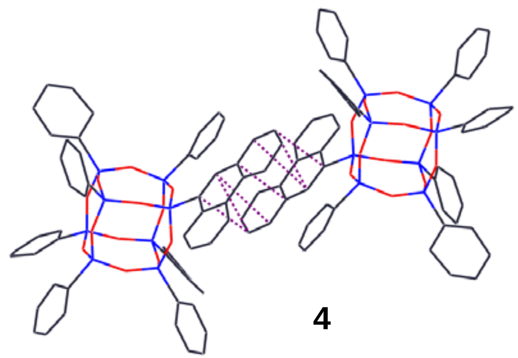








1



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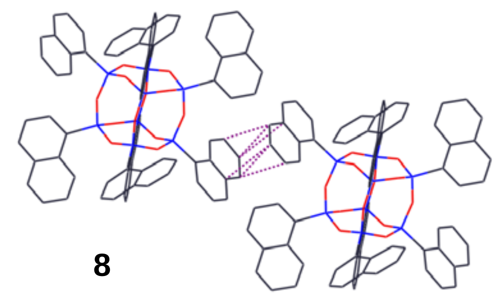
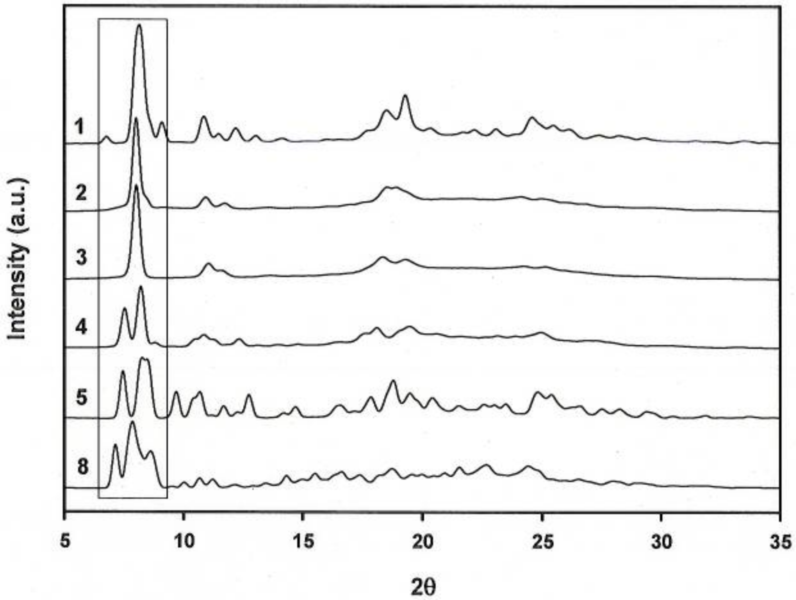
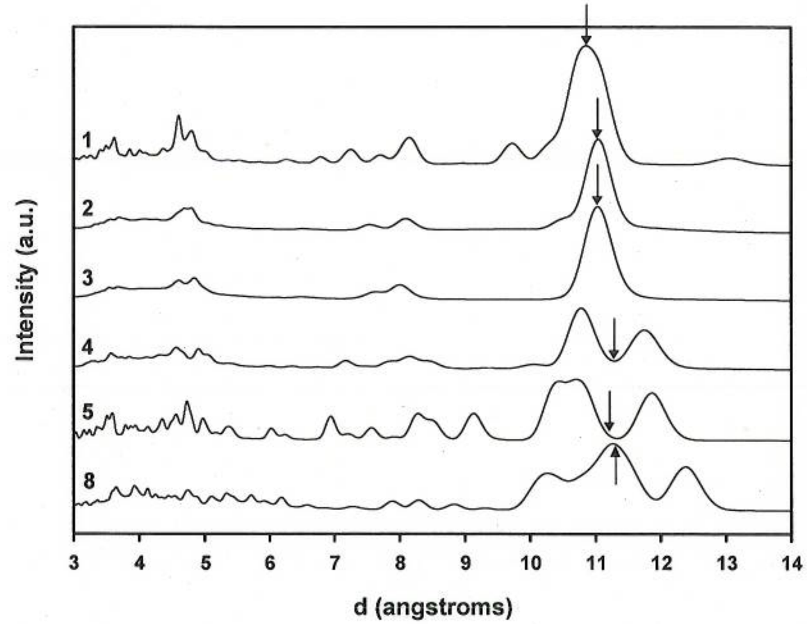


8

- Single crystals solution grown of 1, 4, 5 and 8
- The unit cells of all of the compounds are monoclinic
- Aromatic interactions are prevalent for all of the resolved structures

Powder XRD





- Peaks of strongest intensity occur between 5 and 10° 2θ - likely correspond to periodicity in POSS cages
- Average distance between POSS cages appears to increase with size of peripheral species

Modulated DSC

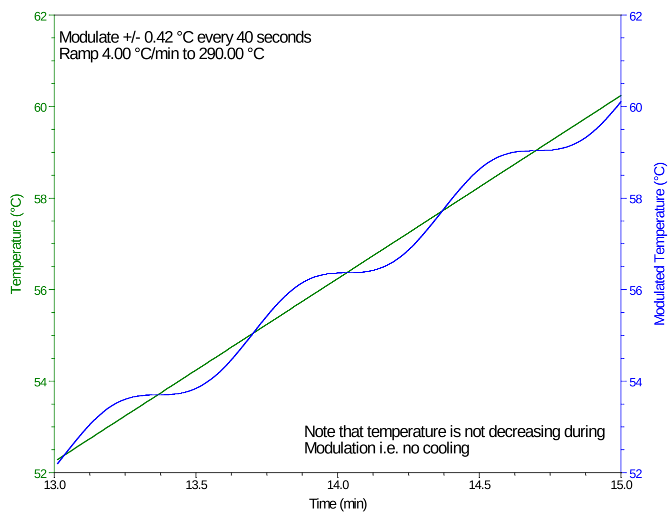
$$\frac{dH}{dt} = Cp\frac{dT}{dt} + f(T,t)$$

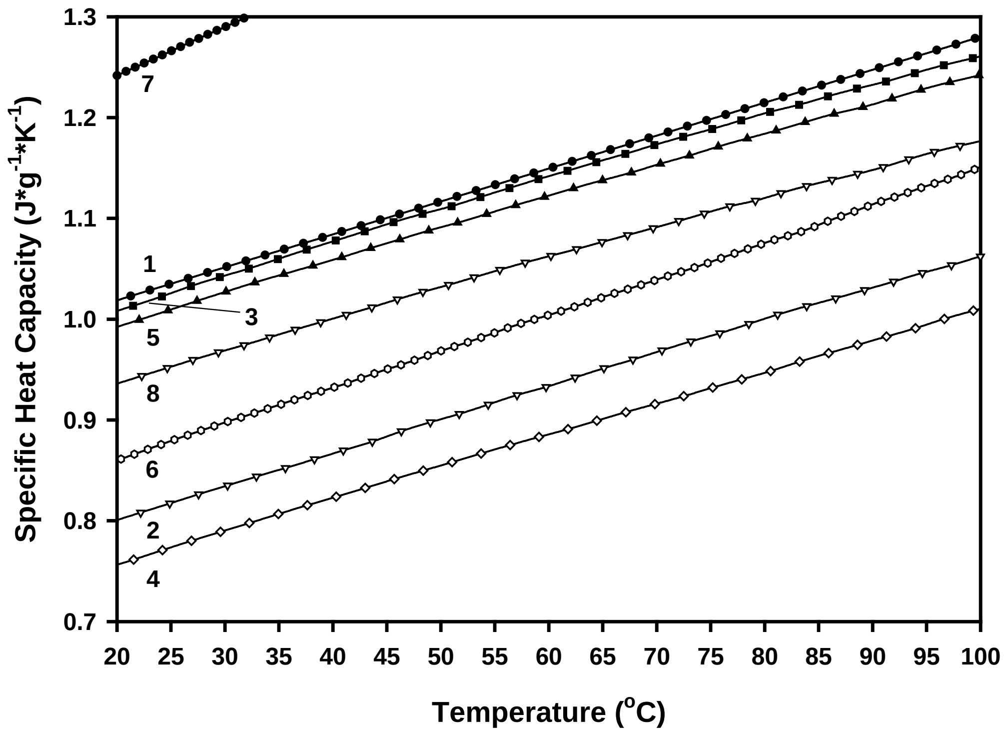
Reversing

Heat Capacity
Glass Transition
Most Melting
Transitions

Nonreversing

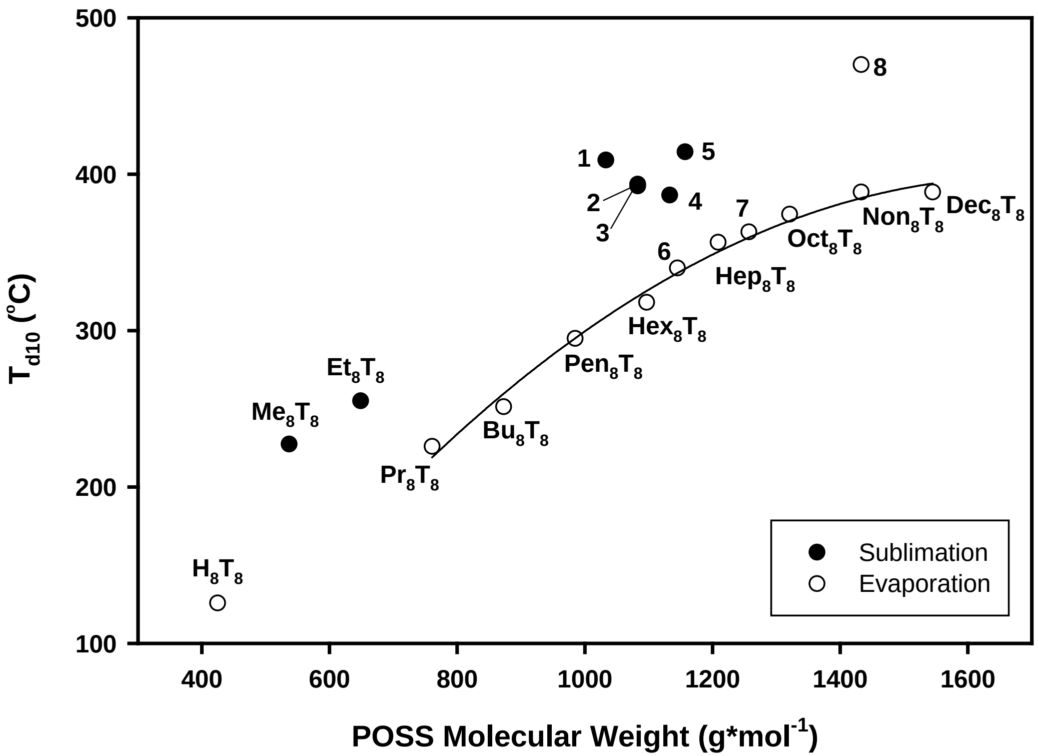
Crystallization
Thermoset Cure
Decomposition





- **Slopes of 6 and 7 greater than those of purely aryl compounds**
- **C_ps of 2-5 seem to correlate with capable motion of peripheral groups (helicopter effect)**

Influence of POSS Periphery on TGA Mass Loss



Data for alkyl POSS taken from:

- Fina, A. T., D.; Carniato, F.; Frache, A.; Boccaleri, E.; Caminoa, G., Polyhedral oligomeric silsesquioxanes (POSS) thermal degradation. *Thermochimica Acta* **2006,** *440*, 36-42
- Bolln, C. T., A.; Frey, H.; Ihaupt, R.M., Thermal Properties of the Homologous Series of 8-fold Alkyl-Substituted Octasilsesquioxanes. *Chem. Mater.* **1997,** *9*, 1475-1479.

- Alkyl POSS compounds that evaporate due so according to their molecular weight (R^2=0.99)
- Weight loss of aryl POSS compounds investigated in this study is more complex due to peripheral interactions

Summary

- **Aryl POSS periphery affects molecular packing efficiency which influences thermal properties such as mass loss and heat capacity**
- **Thermal decomposition of aryl POSS is dependent on packing efficiency, temperature, and heating rate**
- **These findings can be used in the future to tailor thermally stable POSS compounds for specific properties**